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THE NEXT GENERATION OF SILICON-BASED PLASTICS: POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) NANOCOMPOSITES

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INTRODUCTION

The proposed operational requirements of future military, space, and commercial vehicles, have forced designers and engineers to increasingly incorporate light-weight polymeric structures into higher temperature component applications. Consequently, existing hydrocarbon-based resin technology will be pushed to its critical thermal performance limits while material performance issues such as reduced flammability and retention of mechanical properties at elevated temperatures have not been satisfactorily resolved. Despite manufacturers' and molders' attempts to obtain new physical properties from the existing pool of polymer types, the low cost avenues of polymer-polymer blending and processing manipulations have only produced incremental improvements to properties. Surprisingly the development of new chemical feedstock technologies that may offer high-tech solutions to inherent material-property shortcomings have not been seriously pursued.

In attempt to meet its demand for a new generation of lighter weight and higher performance polymeric materials, the US Air Force has for the past decade pursued the development of a new chemical feedstock technology based on Polyhedral Oligomeric Silsesquioxanes (POSS). POSS chemical technology is derived from the same silane feedstocks that are currently used to prepare conventional bulk silicone resins.¹ However, the technology is unique in that POSS-reagents are physically large, three-dimensional cages (approx. 15 Å diam. and 1000 amu) that are nearly equivalent in size to most polymer dimensions, and their composition is a hybrid (intermediate between inorganic and organic) (*vide infra*). Recently bulk-scale preparative methods and a catalogue of POSS monomers (new chemical feedstocks) have been established.

POSS-Chemical Tree

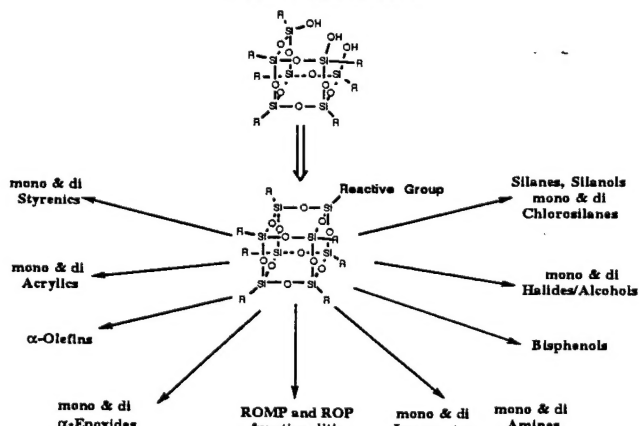


Figure 1. Chemical diversity of POSS-nanostructured monomers/reagents.

POSS technology can be utilized as comonomers, or as graftable agents while POSS-polymers and copolymers can be utilized as either blendable or moldable resins. The chemical nature of POSS reagents and copolymers allows the technology to be easily incorporated into existing material formulations and it can even be tailored for compatibility through manipulation of the solubilizing/nonreactive organic groups (R) located on each of the cages.^{1,2}

RESULTS AND DISCUSSION

To date we have incorporated POSS structures into glassy, liquid crystalline, semicrystalline, and elastomeric polymer types. The mono and difunctional POSS reagents developed by the USAF have been demonstrated to be amenable for use in thermoplastics, sol-gel, and in conventional thermoset systems. The scope and range of property enhancements in POSS-based nanocomposite plastics are only now beginning to be identified. Despite a dependence on composition, polymer type, and architecture, a few

general property enhancement trends have become apparent. POSS incorporation effectively reduces polymer flammability,³ decreases thermal conductivity, improves oxidation resistance,⁴ increases permeability to gases,⁵ increases glass transitions,⁶ improves heat distortion and melt strengths,⁷ and significantly increases moduli. Although highly dependent upon processing, molding conditions, and composition, the tensile properties of POSS-plastics are observed to be nearly equivalent to those of the parent organic resin. Interestingly nanocomposites derived from POSS do not appear to suffer from decreases in shear strengths as do the exfoliated/intercalated clay-based nanocomposite systems.⁸

In an attempt to understand the fundamental nature of nanoreinforcement and property enhancement in these systems, we have undertaken studies aimed at probing the solid-state structure of POSS monomers and the linear POSS-bead, POSS-pendant, POSS-triblock, and POSS-star polymer architectures.⁹

Single crystal studies on the exodisilanol monomer ($c\text{-C}_6\text{H}_{11}\text{Si}_8\text{O}_{11}(\text{OH})_2$) provide insight into the volume requirements, packing arrangement, and the maximum density obtainable for POSS monomers bearing cycloaliphatic groups. Based on the single crystal data of silanols reported by Lickess and others,¹⁰ it is not surprising to observe that in the solid state this disilanol monomer adopts a hydrogen-bound polymeric structure with a distance of 2.98 Å between the two hydrogen-bound oxygens. The POSS disilanol monomers pack in a staggered arrangement wherein POSS cages in adjacent layers lie between the two hydrogen bound portions of cages in the adjacent layers. Multiple Van der Waal associations are also observed between the cyclohexyl substituents between adjacent layers. While individually such non-bonding interactions are very weak, collectively they may contribute significantly to interactions between POSS cages or between POSS and polymer segments.¹²

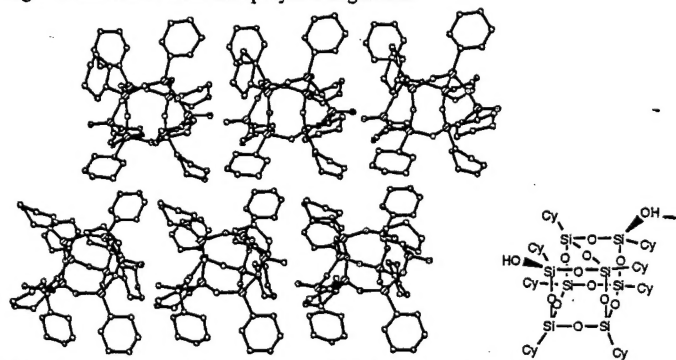


Figure 2. Packing of the exodisilanol ($c\text{-C}_6\text{H}_{11}\text{Si}_8\text{O}_{11}(\text{OH})_2$).

Despite the close resemblance of POSS reagents to silica, the volume occupied by the solubilizing organic substituents on the cage significantly reduces the relative density of these systems. For example the crystal density for the exodisilanol is only 1.21 g/ml as compared to that of 2.19 g/ml for vitreous silica. The density of POSS monomers is also in agreement with the measured densities of 1.12 g/ml for POSS-siloxane bead-type copolymers with 70-90 wt. percentage incorporations of this same monomer.¹¹

Comparison of the X-ray powder diffraction spectra of the ($c\text{-C}_6\text{H}_{11}\text{Si}_8\text{O}_{11}(\text{OH})_2$) monomer to that for two corresponding POSS-siloxane bead-type copolymers reveals the highly amorphous nature of these copolymers. Amorphous diffraction patterns are also observed for POSS-siloxane copolymers with pendant-POSS architectures. However, triblock and star architectures show crystalline and amorphous diffraction patterns. The crystallinity is, however, highly dependent upon the number of POSS groups incorporated into the structure and on the length of the amorphous segments between the POSS groups.¹³

The two POSS-siloxane copolymers in Figure 3 differ only in the number of dimethylsiloxane units separating the POSS cages. The two diffraction maxima observed are thought to correspond to inter and intrachain spacings between the POSS cages. While we are currently re-examining the validity of such an assignment, it has reportedly been confirmed by Zhang in related polymeric silsesquioxane resin systems.¹⁴

Interestingly, the diffraction maxima for the copolymer with a single dimethylsiloxane segment between each cage shows the largest span in d spacings (11.08 Å and 4.90 Å). While the copolymer containing

oligomeric PDMS segments between cages shows diffraction maxima which are closer together in d spacing (10.76Å and 4.96Å). This suggests that the longer and presumably more flexible PDMS segment facilitates the packing of the POSS cages relative to one another as compared to the case in which the POSS cages are linked by a short and less flexible single dimethylsiloxane segment. Further discussion for these and related systems will be forthcoming.

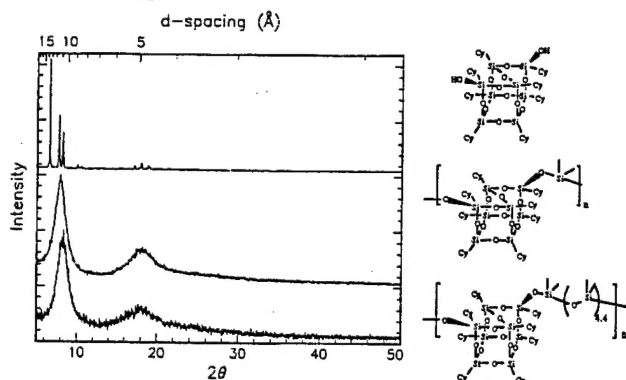


Figure 3. Powder diffraction patterns for a monomer and two copolymers.

Of equal importance to studying the solid state structure of POSS nanocomposites are experiments which examine their viscoelastic properties. We have carried out such work on a large number of POSS-reinforced plastics and of particular interest has been the observation of the reinforcement of modulus at specific critical POSS concentrations. For example, the plot of storage modulus versus frequency in Figure 4 shows that the parent (0%POSS) and 4wt% POSS copolymers are below the effective entanglement molecular weights however, increasing the percentage of POSS in this system results in effective reinforcement of the polymer chains. Thus as the POSS content in the copolymer is increased the copolymer begins to show rubbery properties. Increases in POSS content from 8 to 16 % results in further increases in the value of the plateau modulus. This result suggests that POSS-nanostructures can reinforce polymer chains and hence alter physical properties. Further discussion of these studies will be forthcoming.^{7a}

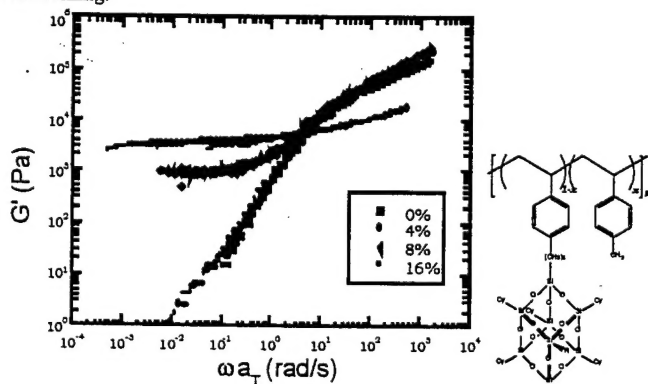


Figure 4. Rheological properties of POSS-Styryl copolymers.

In attempt to understand, the nature and magnitude of physical property enhancements possible in POSS-nanocomposites, we have pursued the development of a conceptual/predictive model of such systems. Based upon the packing arrangement observed from the single crystal X-ray diffraction studies and on the structure inferred from the powder diffraction and rheological experiments, we propose the following conceptual model for a 50-70 vol % POSS-nanocomposite (Figure 5).

In such a system coil-coil and segment-segment interactions no longer dominate instead, POSS-POSS interactions dominate the continuum and hence control physical properties in the material. Given that POSS-cages themselves are not as susceptible to thermal motion¹⁵ as are polymer segments and given the inherent oxidative stability of the POSS nanostructures¹⁶ such polymers could be expected to be more oxidatively stable and to retain more of their mechanical properties at elevated

temperatures. Chain motion in such nanoreinforced systems would also be retarded (hence unprecedented increases in T_g ^{6b}) and compression/creep properties may also be improved. Further refinement of this model via experimental and theoretical methods is currently underway.

POSS-Polymer Chain Model

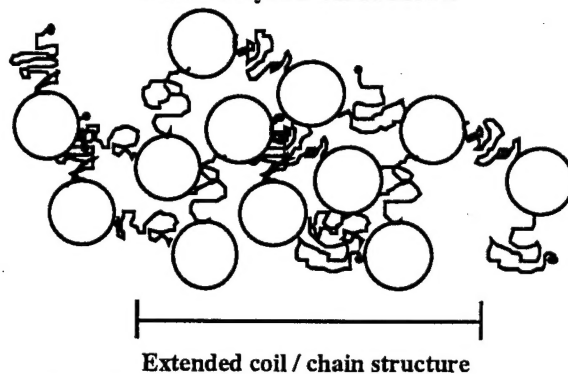


Figure 5. Conceptual model for POSS-nanocomposites.

EXPERIMENTAL

X-ray powder diffraction measurements were performed using a Scintag D5000 theta-theta diffractometer system using Ni filtered Cu K-alpha radiation (1.5406Å). Samples were ground to 200 mesh (74μ) and thinly spread onto a zero-background plate. All materials were prepared following literature methods^{11,17} and were prepared by precipitation from THF into methanol and drying under vacuum.

Single crystal studies on $(\text{C}_6\text{H}_{11})_8\text{Si}_8\text{O}_{11}(\text{OH})_2$ were performed using a Siemens P4 diffractometer and the structure was solved in the $P2_1$ space group with unit cell dimensions of 10.366 x 21.500 x 14.429Å. The data set refined to $R = 27\%$, $R_w = 38\%$ and a GOF = 1.031.

CONCLUSIONS

The preliminary studies into the solid-state and viscoelastic properties of POSS-based nanocomposite hybrid plastics suggest that POSS-POSS interactions may have a dominant role in controlling the chain structure, motion and resulting physical properties. Experimentally, nanosized POSS structures appear to enhance physical properties by providing localized structure (nanoreinforcement) to polymer chains/segments.

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